

PATENT SPECIFICATION

762,421



Date of Application and filing Complete Specification:
July 6, 1954.

No. 19716/54.

Application made in Germany on June 19, 1954.

Complete Specification Published: Nov. 28, 1956.

Index at acceptance:—Class 2(3), C3A14A(1B : 8D).

COMPLETE SPECIFICATION

Process for the Production of Ketones

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of Homberg/Niederrhein, Germany, a German company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a process for the production of ketones, particularly aliphatic ketones containing from 4 to 6 carbon atoms in the molecule.

15 In most cases, ketones are produced by the de-hydrogenation or oxidation of secondary alcohols. Ketones are also produced by the thermal decomposition or dry distillation of the calcium salts of fatty acids. In the production of complicated ketones, it has hitherto been necessary to react acid chlorides or nitriles with Grignard compounds, or to subject esters of carboxylic acids to condensation with compounds which contain reactive methylene or methyl groups.

25 It has now been found that monomethylol compounds of aliphatic C_4 to C_6 ketones, in which the keto and hydroxyl groups are in 1.3 position relatively to each other, may be reduced in a smooth reaction with hydrogen to form the corresponding ketones by using an elevated temperature and elevated pressure in the presence of catalysts which have a dehydrating and hydrogenating action. 30 The reaction is carried out in such manner that the reduction occurs solely at the methylol group while the keto group remains unaffected.

40 According to the invention, a process for the production of an aliphatic ketone comprises reducing an aliphatic 1.3-keto-alcohol containing from 4 to 6 carbon atoms in the molecule with hydrogen at a partial hydrogen pressure in the range 1-100 atmospheres and at a temperature in the range

100°-200°C. in the presence of a catalyst having a dehydrating and a hydrogenating effect.

According to the invention furthermore, a continuous process for the production of an aliphatic ketone comprises suspending a catalyst active for dehydration and hydrogenation in an aliphatic 1.3-keto-alcohol containing from 4 to 6 carbon atoms in the molecule, passing hydrogen through the suspension at a pressure in the range 1 to 100 atmospheres, and maintaining the suspension at a temperature within the range 100°-200°C.

60 The reduction of the keto-alcohols is dependent upon the temperature and the pressure used. The reduction commences at approximately 100°C. and is advantageously continued at temperatures in the range 140°C.-170°C. Above 200°C. side reactions occur. Practically no diol is formed when low pressures are employed. With increasing pressures the tendency to form diols increases, particularly at partial hydrogen pressures greater than 100 atmospheres. The hydrogen pressure preferably lies in the range 10-20 atmospheres, at which pressures the rate of reaction is adequate whilst the formation of an appreciable quantity of diols is avoided.

75 The catalyst used, which may, if desired, be a mixture of catalysts, is a compound or a mixture of compounds having a dehydrating and a hydrogenating effect or action. It has been found to be advantageous to use catalysts which consist of mixed metal oxides, such as copper oxide-chromium oxide, or zinc oxide-chromium oxide, or combinations of dehydrating and hydrogenation catalysts, such as aluminium oxide, silica gel, or pumice on the one hand, and nickel catalysts on the other. The catalyst may be used as a stationary or fixed bed, for example, it may be disposed in the tubes of a pipe or tube reactor, or it may be sus-

(Price 3s. 0d.)

Price 4s. 6d.

pended in the keto-alcohol which is to be converted. Moreover, the walls of the reactor may be lined with materials which have a catalytic effect.

- 5 The feedstocks used for the production of ketones are those C_4 - C_6 keto-alcohols in which the keto and hydroxyl groups are disposed in 1,3 position relatively to each other, for example, 3-ketobutanol-1 CH_3 -
 10 $CO-CH_2-CH_2-OH$, 2-methyl-3-ketobutanol-1 $CH_3-CO-CH(CH_3)-CH_2OH$, 2-ethyl-3-ketobutanol-1 $CH_3CO-CH(C_2H_5)-CH_2OH$ and 2-methyl-3-ketopentanol-1 $CH_3-CH_2-CO-CH(CH_3)-CH_2OH$. It has been found to be particularly advantageous to use for the catalytic reduction a keto-alcohol obtained by the condensation of an aliphatic ketone with formaldehyde. The keto-alcohols thus obtained are distinguished by particular purity,
 15 which in turn facilitates the production of ketones by the process according to the invention, since any tendency to the occurrence of side reactions is thereby further suppressed.
- 25 The process according to the invention may be carried out in a particularly advantageous and simple manner in continuous operation. For this purpose, apparatus known for carrying out conversions in the liquid phase may be used, for example, the
 30 reaction apparatus used to carry out the Fischer-Tropsch synthesis in the liquid phase. The catalyst, suspended in the keto-alcohol to be converted, is disposed in the reactor which is capable of being cooled and heated. Hydrogen is introduced from below into this suspension. It is advantageous to use an excess of hydrogen, which can then be used as a carrier gas for the water
 35 and ketone vapours evolved during the reaction, and which is or can be returned to the reaction space after separation of the water and of the ketone. From the top of the reactor a tail-gas or outlet pipe extends through a condenser into a receiver for the condensed product. This pipe system must be well heated to its culminating point in order to facilitate the distilling-over of the reaction products. The quantity of fresh
 45 keto-alcohol added continuously to the suspension in the reactor should be substantially equivalent to the ketone and water which distills off from the suspension. In view of its simplicity, this continuous method of operation is superior to a batch-wise method of operation, inasmuch as the time-wasting operations of charging and discharging, heating and cooling, as well as the difficult operation of separating the catalyst from the reaction product, are
 50 avoided.

65 It is known to hydrogenate keto-alcohols catalytically into diol compounds. It is also known to reduce ketones to secondary alcohols in the presence of copper-chromium

oxide. It is, therefore, surprising that under the reaction conditions used in accordance with the invention, it is possible to hydrogenate the vinyl group formed as an intermediate by the elimination of water whilst the keto group is unaffected.

The invention is illustrated by the following examples:—

Example 1

75 A copper-chromite catalyst was used, the catalyst having been prepared as follows:— The metal carbonates were precipitated from a solution of 50 grams of copper nitrate, 5.4 grams of barium nitrate, and 77 grams of chromium nitrate in 575 cc. of water by adding 100 grams of ammonium carbonate dissolved in 400 cc. of water. The precipitate was removed by suction-filtration, washed twice using 50 cc. of water each time, dried at $100^\circ - 110^\circ C$, pulverised, and decomposed at $230^\circ C$.

130 grams of 3-ketobutanol-1 and 13 grams of the copper-chromite catalyst were placed in an autoclave provided with a shaking mechanism. After hydrogen had been introduced under a pressure of 40 atmosphere gauge, the autoclave was heated with constant shaking to $150^\circ C$. and maintained at $150^\circ - 160^\circ C$. After $1\frac{1}{2}$ hours the pressure in the autoclave had dropped to 18.7 atmospheres gauge. After cooling of the autoclave to room temperature, the pressure was released and the reaction mixture was separated from the catalyst. The reaction mixture contained 77% by volume of methyl ethyl ketone, which corresponds to a conversion of almost 93%.

Example 2

The autoclave was charged with 447 grams of 2-methyl-3-ketobutanol-1 and 45 grams of the copper-chromite catalyst hereinbefore described, which catalyst had previously been used in three hydrogenations. After the introduction of hydrogen under a pressure of 30 atmospheres gauge, the autoclave was heated with constant shaking to $150^\circ C$, and a temperature of from $150^\circ - 160^\circ C$. was maintained. When the overall pressure in the autoclave had dropped to 20 atmospheres gauge, hydrogen under pressure was repeatedly introduced to bring the total or overall pressure to 45 atmospheres gauge. The reaction was substantially complete after the heating at $150^\circ - 160^\circ C$. had been continued for $3\frac{1}{2}$ hours. When the autoclave was absolutely cold, the pressure was released and the autoclave was emptied, the liquid reaction mixture being separated from the catalyst and subjected to fractional distillation. 61% by volume of methyl isopropyl ketone and 14.5% by volume of unconverted 2-methyl-3-ketobutanol-1 were obtained. Based on the keto-alcohol converted, the yield of methyl isopropyl ketone corresponds to a conversion of 84%. This

example demonstrates the long active life of the catalyst used.

What we claim is:—

1. A process for the production of an aliphatic ketone, which comprises reducing an aliphatic 1.3-keto-alcohol containing from 4 to 6 carbon atoms in the molecule with hydrogen at a partial hydrogen pressure in the range 1-100 atmospheres and at a temperature in the range 100°-200°C. in the presence of a catalyst having a dehydrating and a hydrogenating effect.

2. A continuous process for the production of an aliphatic ketone, which comprises suspending a catalyst active for dehydration and hydrogenation in an aliphatic 1.3-keto-alcohol containing 4 to 6 carbon atoms in the molecule, passing hydrogen through the suspension at a pressure in the range 1 to 100 atmospheres, and maintaining the suspension at a temperature within the range 100°-200°C.

3. A process according to claim 2, in which a quantity of the keto-alcohol which is substantially equivalent to the ketone and water which distills off from the suspension, is continuously added to the suspension.

4. A process according to claim 2 or claim 3, in which the excess hydrogen is recycled.

5. A process according to any one of the preceding claims, in which the pressure of

the hydrogen is within the range 10-20 atmospheres.

6. A process according to any one of the preceding claims, in which the temperature is within the range 140°-170°C.

7. A process according to any one of the preceding claims, in which the 1.3-keto-alcohol is one obtained by the condensation of an aliphatic ketone containing from 3 to 5 carbon atoms in the molecule with formaldehyde.

8. A process according to any one of the preceding claims, in which the catalyst is a copper-chromite catalyst.

9. A process for the production of an aliphatic ketone containing from 4 to 6 carbon atoms in the molecule, which comprises the reduction of an aliphatic 1.3-keto-alcohol containing from 4 to 6 carbon atoms in the molecule substantially as hereinbefore described.

10. A process for the production of an aliphatic ketone containing from 4 to 6 carbon atoms in the molecule, substantially as hereinbefore described with reference to any one of the Examples.

11. Ketones whenever obtained by the process claimed in any preceding claim.

EDWARD EVANS & CO.,

14-18 High Holborn, London, W.C.1.,

Agents for the Applicants.